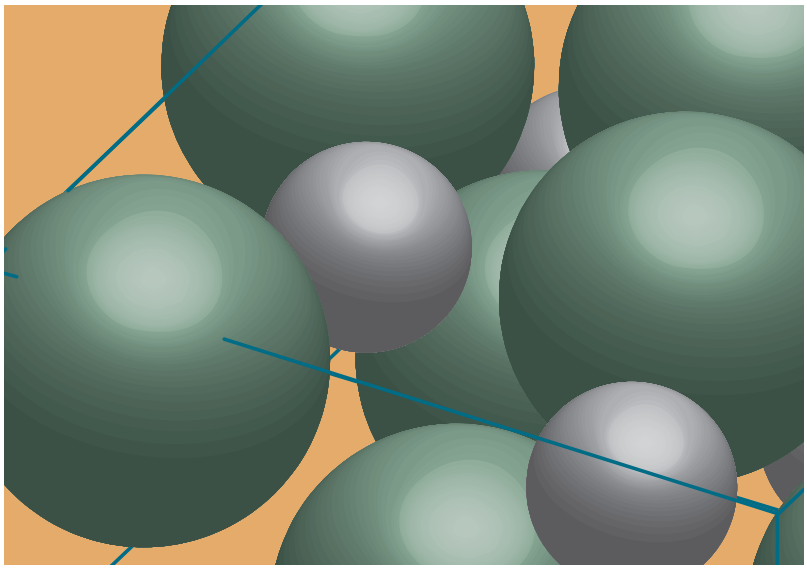
Predicting the Structural and Electronic Properties of Scintillators



We are modeling the properties of scintillators and related materials so that we can guide the synthesis of new materials with improved radiation detection capabilities.

FOR numerous applications, detecting high-energy gamma and x-ray radiation is valuable. Examples include:

- Distinguishing brief showers of secondary particles from infrequent events, such as cosmic rays passing through the earth.
- Monitoring the radiation dose to a patient undergoing medical tomography.
- Identifying sources that may threaten the environment or the safety and health of the public.
- Seeking out covert nuclear weapons.

However, because high-energy radiation cannot be directly detected efficiently, it is more convenient to convert it into photons in the visible or ultraviolet range. These photons can then be readily detected and counted by such means as a photomultiplier. A necessary step in the detection process then becomes the means to convert the high-energy radiation into visible light. Scintillators, materials that emit flashes of light in response to ionizing radiation, are used for just this purpose (see Figure 1).

In the detection process (Figure 2), the incoming radiation interacts with the scintillator's electrons and loses energy by creating electronic excitations in the crystal. These excitations then decay, leading to the emission of photons in the visible or ultraviolet range.

Scintillators are typically wide-gap insulators, such as ionic salts, in which the primary electronic excitation is the creation of electrons and holes (the absence of electrons in normally filled electron states). The size of the energy gap between the empty and filled electron states greatly influences the frequency of the light emitted; a wider gap corresponds to a higher frequency of light. Scintillator materials are often dense, containing deep multi-electron cores (as in the case of barium, lead, and bismuth),

and have many electrons that can produce many excitations. Sometimes, they are even deliberately doped with impurity atoms to create defects that can enhance the radiative decay of electron–hole pairs.

We are modeling the properties of scintillators and related materials like phospors for the purpose of guiding the synthesis of new scintillators. These new scintillators should have a high density of electrons to absorb energy and a fast and efficient luminescence (light emission) to ensure high sensitivity and time resolution. They should also be transparent enough at relevant emission wavelengths to allow the light to pass unattenuated to the detector, and "hard" enough to resist radiation damage by the detected particles after extended use.

Although we can already calculate some of the properties of new materials, we are also studying known materials in order to enhance our predictive capabilities and thereby more accurately model new materials before they are synthesized. For example, we could calculate defect properties, including accurate excitation spectra, to compare with optical absorption and emission measurements in order to identify unknown and troublesome defects in a new material. We could also model useful impurity defects, which would be introduced deliberately into the material.

Modeling a scintillator material is a two-part strategy. First, we determine the material's structural and electronic properties—that is, its atomic structure as a function of density and its electron excitations versus structure, including, for example, electron band structures and electron–hole interactions. Then we use these properties to predict whether a material will be suitable for a particular application or will have characteristics that render it useless.

Structural properties are important because they affect a material's absorption and emission characteristics and its response to heat, pressure, and other external and internal forces. Applying pressure to a material induces volume compression, distortion, and changes in strength, density, and the microscopic arrangement of atoms. Structural changes such as these in turn cause changes in the electron states. The most important electrons are those in the atoms' more energetic outer orbits that are shared among the material's many atoms. To calculate the dynamics of these itinerant electrons (the electron band structure), we must determine the allowed quantum-mechanical states available to them. To do this, we use computational methods based on a model called the local-density approximation (LDA). These methods, together with subsequent corrections to the LDA model—such as those describing electron–electron interactions in more detail—also help us to determine electron–hole interactions and to predict how various materials will function as scintillators.

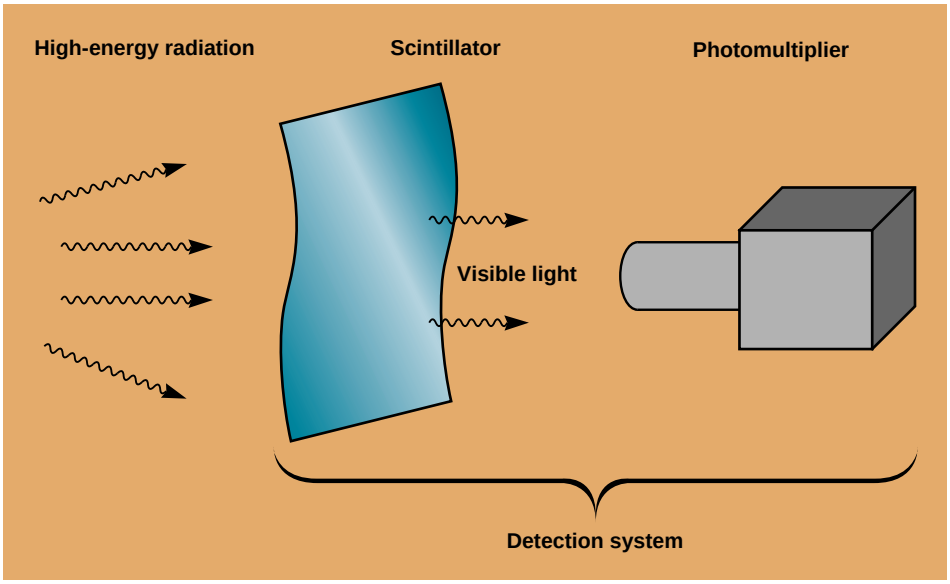


Figure 1. Scintillators are used to convert high-energy radiation into visible or ultraviolet light. These photons can then be readily detected and counted by such means as a photomultiplier.

The Local Density Approximation Model

Computational methods based on the LDA model can be used to determine both the atomic and electronic structures of materials, including potential scintillator materials such as lead fluoride, barium fluoride, the cesium halides, and lithium fluoride. For example, these methods can be used to determine properties such as a material's crystal structure (e.g., cubic or orthorhombic) and density, internal atomic coordinates, possible structural phase transitions, and associated transition pressures. They can also be used to describe the atomic structure near a defect and, very importantly, the relation between a material's structure and its electronic properties. In contrast to the atomic structure, the electronic structure

deals primarily with the dynamics of electrons in a solid, specified by the wave functions and energies of the electron states.

Determining Scintillator Structure

To determine the atomic structure of a scintillator, or any other material, we determine the total energy of its electrons and then minimize that total energy with respect to the atomic coordinates and crystal unit-cell dimensions. To determine the total energy, we first consider each electron separately, treating it as if it were moving in an average potential field created by all the remaining negative and positive charges in the crystal. We then apply a unique functional of the electron density, obtained from a sum over all the electrons, which yields the material's total energy. Although the exact form of this functional is unknown, we can get an exceptionally accurate and practical approximation to it using the LDA model.

We currently have two very accurate LDA-based methods for treating the motion of electrons—the pseudopotential method, which applies only to the valence electrons in a solid and therefore to its "pseudo" nuclear potential, and an all-electron method, which applies to all electrons in a solid and therefore to its true nuclear potential.

The Pseudopotential Method

The pseudopotential method eliminates the atom's deeply bound core electrons and the potentials that bind them, allowing us to focus solely on the relevant structural, electronic, and optical properties of the valence electrons, which are the ones active in the chemical bonding of materials. This method also allows us to employ powerful mathematical tools (such as Fourier analysis, where the electron wave functions are described in terms of plane waves) to study problems at the small cost of slight approximations.

Although the pseudopotential method simplifies the description of the valence electrons, we use psuedopotentials that are norm-conserving; they leave this description unchanged in the chemically important bonding regions. Such norm-conserving pseudopotentials are highly transferable; that is, they can be used to predict the chemistry of an atom in a wide range of situations (e.g., bulk, surface, adsorbate). Because norm-conserving pseudopotentials do not rely on prior experimental knowledge about a chemical element, we can construct one for every element in the periodic table.

All-Electron Methods

When the pseudopotential approximation is not sufficiently accurate for a material, as is the case with some transition metal and actinide elements (some of which are candidate scintillator materials), we can use all-electron methods that explicitly treat both the deep and shallow core electrons as well as the valence electrons.

All-electron methods work equally well regardless of the degree to which the electron states are localized or extended; therefore, they are immediately applicable to a wide range of materials. They are also useful for materials whose relevant

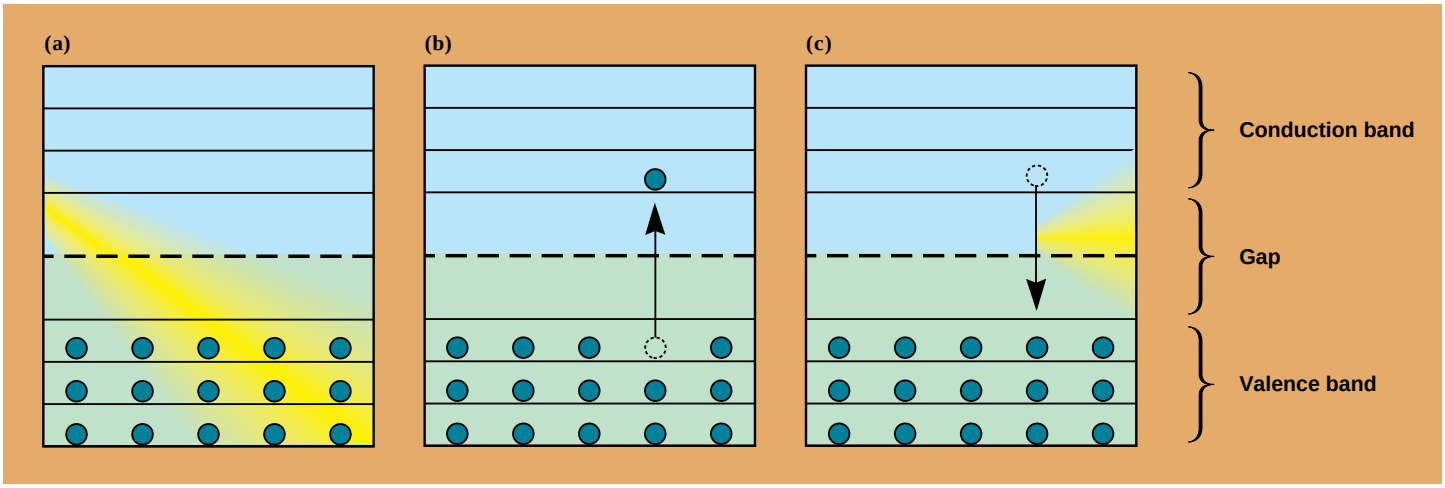


Figure 2. Schematic of the scintillation process. (a) Incoming radiation (such as light) enters a crystal. Note the filled (low-energy) and empty (high-energy) states of electrons delineated by the Fermi energy (dashed line). (b) The radiation absorbed by the crystal excites its electrons (one promotion shown) from filled to empty states. (c) When the electrons later become de-excited, the electron and hole in (b) recombine, and readily detectable radiation is emitted from the crystal.

properties depend specifically on the core electrons and for materials at pressures where the shallow core electrons of the compressed atoms may participate in the chemical bonding.

All-electron methods are also computationally efficient for systems with small numbers of atoms. However, they are mathematically complex and not as amenable to the mathematical tools used in conjunction with pseudopotentials. One consequence of this complexity is a rapid degradation of computational efficiency for complicated structures. The pseudopotential method is usually more efficient for systems such as surfaces, interfaces, and defect structures. On the other hand, the description of the electronic wave functions obtained from all-electron calculations is more convenient for identifying the chemical nature of the electronic states. Chemical analyses of these states often provide important insights into the properties of materials such as scintillators. Ultimately, the benefit of having expertise with both pseudopotential and all-electron methods is that we can use the most suitable method for any given problem. In this way, the methods complement each other. They also serve as a check on each other when both are applicable.

Describing Electron–Electron Interactions

The LDA model treats each electron as being approximately independent from all other electrons, but they are, in reality, not independent. An electron or hole polarizes a material by interacting with other electrons. Some induced polarization also occurs as other electrons move away from a given electron, creating a polarization cloud that changes the energy of the electron. This change, which occurs for all electronic states, is called the self energy. Although self-energy effects are approximately included in the LDA model, the proper way to treat such effects is by means of a quasiparticle approach. A quasiparticle can be either an electron plus its polarization cloud or a hole plus its polarization cloud. These effects are critical for an accurate treatment of electronic excitations, but the LDA model is more than adequate for treating most structural properties.

To appreciate the differences in accuracy between the LDA and the quasiparticle approaches, one has only to look at lithium fluoride, a luminescent insulator that has the widest known band gap of any material except artificial systems such as noble-gas solids (Figures 3 and 4). Experiments indicate that lithium fluoride has a band gap of 14.1 to 14.2 eV between its conduction and valence bands. The width of the fluorine valence-band is approximately 3.5 eV. The shallowest fluorine core electrons lie roughly 21.5 eV below the valence-band maximum. According to the LDA model, the band gap is 8.9 eV, the valence bandwidth is 3.1 eV, and the core electrons are 19.5 eV below the valence–band maximum. On the other hand, the quasiparticle results, which are considerably better than the LDA results, yield a band gap of 14.2 eV, a valence bandwidth of 3.7 eV, and a centroid for the core electron band that is 21.5 eV below the valence-band maximum.

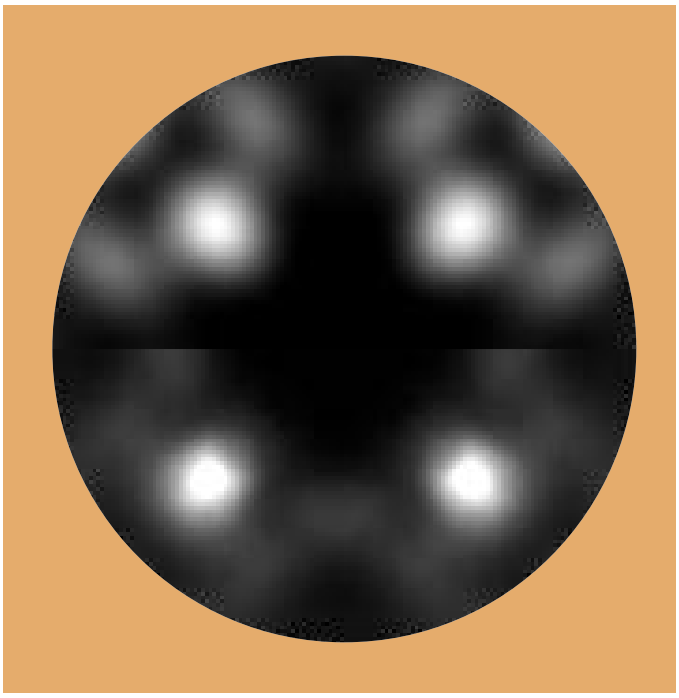


Figure 3. Experimental (top half) and simulated (bottom half) angular distribution patterns for photoelectrons excited from a lithium fluoride crystal. Areas of high electron intensity appear brighter. The two patterns, which show significant correspondence, would appear indistinguishable if the theory and experiment agreed perfectly.

Describing Electron–Hole Interactions

If we want to describe the excitations in scintillators, we need to do more than describe just one electron or one hole even within the quasiparticle approach. We need to describe electron–hole interactions since the important electronic excitations are electron–hole pairs. When one of these electron–hole pairs decays in a radiative process, scintillation occurs. Such decay occurs when an electron falls into the hole state, refilling the vacancy left by a previous electron. It can also occur during atomic motion, as a nonradiative

process, or during the emission of light, as a radiative process.

In the case of electron–hole pairs, we also need to describe the coupled motion of the two particles (electron and hole) and are already working on approaches to do just that. For instance, the same theory that has been applied to fullerene solids[1] (which are not scintillators) can also be applied to scintillators.

Current Projects

We have used our all-electron LDA method to calculate the atomic structure of barium fluoride and lead fluoride, both of which can exist in one of two phases (either cubic or orthorhombic—see Figure 5) at low pressures. The cubic phase is observed to be the most stable (the lowest energy) experimentally, and our calculations reproduce this observation correctly. We have also calculated the pressure at which lead fluoride transforms from the cubic to the orthorhombic phase and find that it agrees with the experimentally measured transition pressure. In the case of the orthorhombic phase, there are a large number of independent structural parameters that describe the atomic structure of the material. Once again, the calculated structural parameters agree well with experiment. This high level of agreement is an example of the quantitative accuracy of LDA calculations and is well documented. Thus, even in the absence of experimental measurements, we can have confidence in calculated structural quantities. This confidence is important because all other properties of a material depend on the atomic structure.

Cubic barium fluoride is known experimentally to be a fast scintillator, whereas cubic lead fluoride has not been observed to scintillate. However, there is some controversy as to whether the orthorhombic form of lead fluoride luminesces. To address this controversy and to provide insight into the materials properties that distinguish efficient and poor scintillators, we have calculated the electronic band structures of both forms of barium fluoride and lead fluoride. The calculated energy bands for cubic barium fluoride, as well as the chemical nature of the electron wave functions, are consistent with the observed luminescence in this material. The calculations for the orthorhombic phase indicate that it should also be a fast scintillator. Those for cubic and orthorhombic lead fluoride again indicate that the energy bands for the orthorhombic phase are very similar to those of the cubic phase; therefore, the luminescence characteristics of both phases should also be very similar. Because our calculations are for pure, defect-free crystals, we believe that any observed scintillation in orthorhombic lead fluoride is likely the result of defects or other structural imperfections.

Future Directions

First-principles, quantum-mechanical methods afford the calculation of the energies of defect excitations in addition to band gaps. This is of great practical interest because the optical

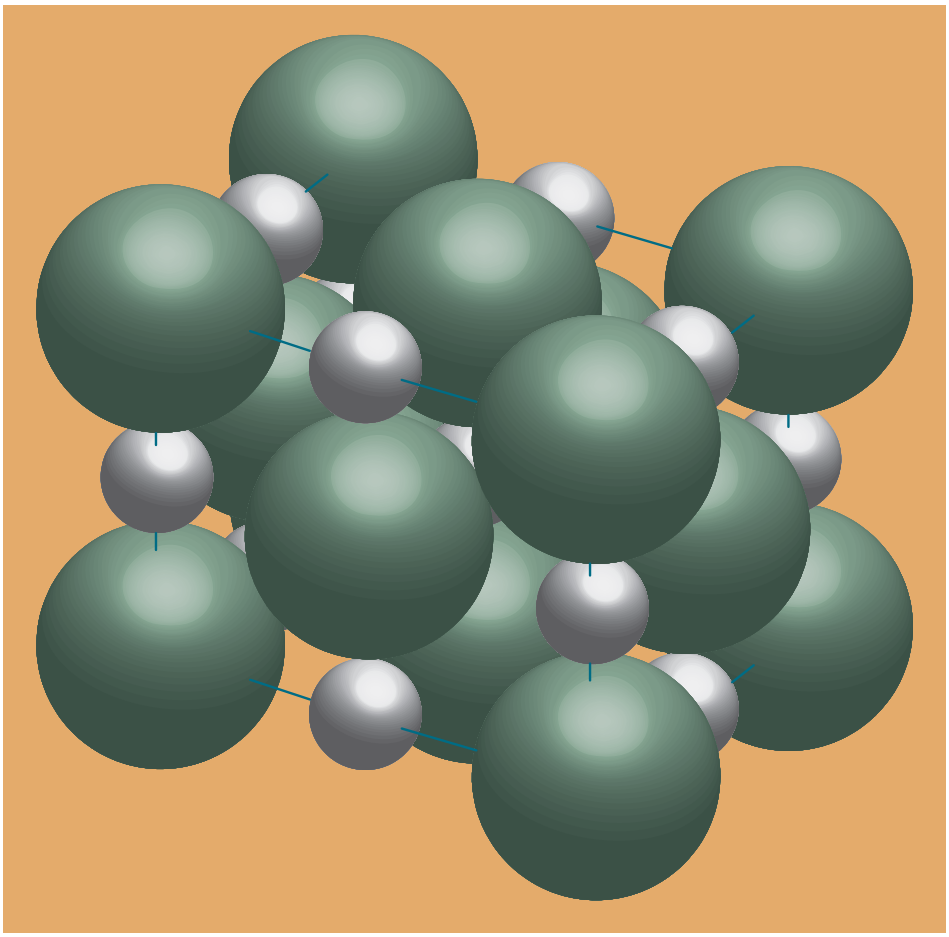


Figure 4. Unit cell of lithium fluoride, which is used for many scintillator and dosimetry applications, including Laboratory dosimeters. The box enclosing the fluorine (green) and lithium (gray) atoms is intended only as a guide.

properties of a material can be tailored by introducing defect levels inside the fundamental band gap. Accidental defects can also degrade the performance of a scintillator. At present, no one can calculate defect excitations accurately, so we have to generalize the quasiparticle method to handle this problem. The first application of this method, to a chlorine vacancy in lithium chloride, yielded an accurate estimate of the frequency of light absorbed by this defect. Eventually, it should be possible to predict defect properties for a wide range of materials, thereby advancing the development of new scintillators.

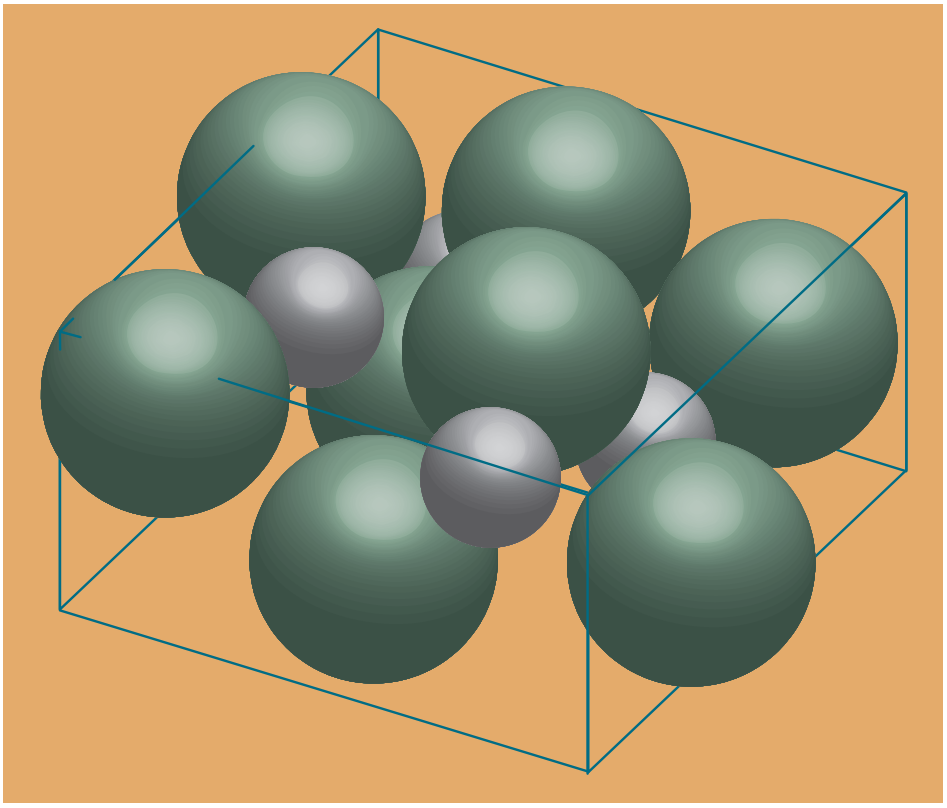


Figure 5. Unit cell of the orthorhombic phase of lead fluoride, which has potential scintillator applications. The connecting lines that define the box enclosing the fluorine (green) and lead (gray) atoms are intended only as a guide.

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Key Words: electrons; local-density approximation; pseudopotentials; quasiparticles; radiation detection; scintillators.

Notes and References

1. All research on fullerene solids had been completed as of the date of this writing, but a document describing the work has not yet been published. For more information on fullerene solids, contact Eric Shirley (301) 975-2349.

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